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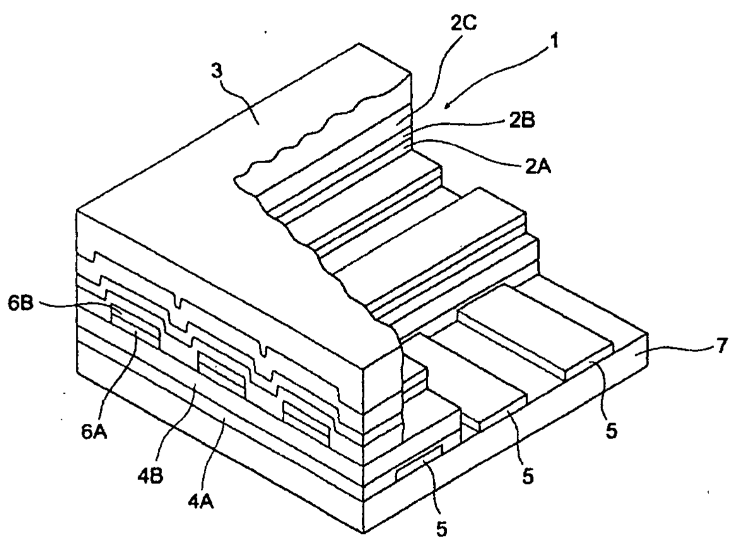
(54) Title: PROTECTIVE ENCAPSULATION FOR ORGANIC ELECTROLUMINESCENT DEVICES



(57) Abstract: An encapsulant for organic electroluminescent devices (4) of the type deposited on a supporting substrate (7) and composed of at least two electrodes (5, 6) between which an electroluminescent substance is arranged, the encapsulant being formed by at least one first inner layer (2), which is in direct contact with the electroluminescent device (4), constituted by an organic compound of the type of quinacridones, acridones, and derivatives of perilene, the organic component being suitable to isolate the electroluminescent device (4) from the atmospheric agents.

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PROTECTIVE ENCAPSULATION FOR ORGANIC ELECTROLUMINESCENT DEVICES

Technical Field

The present invention relates to a protective encapsulation for organic electroluminescent devices.

Background of the Invention

Currently commercially available electroluminescent devices (LED = Light Emitting Diode) are used in the fabrication and provision of displays and video screens. They are constituted by inorganic compounds, which emit visible light if placed between two electrodes to which a voltage is applied.

Although inorganic LEDs have a good performance in terms of emission and duration, they are nonetheless complicated and difficult to fabricate, and accordingly the fabrication of displays based on their use is expensive.

Organic electroluminescent devices, known by the acronym OLED (Organic Light Emitting Diode), are constituted by at least one layer of organic material placed between two electrodes. Generally, these devices are constituted by multiple, different and mutually superimposed organic layers, so as to optimize the electric charge transport and recombination properties with respect to OLEDs constituted by a single layer.

In OLEDs, both the organic layers and the electrodes are sensitive to the deterioration produced by the presence of oxygen and humidity. This deterioration causes the appearance of non-emissive regions.

In these devices, the lack of effective isolation from the outside environment is a severe impediment to their application in commercial devices, such as for example displays.

Disclosure of the Invention

The aim of the present invention is to obviate the above cited drawback by providing a protective encapsulation that is new in concept and isolates and protects both the layers of organic material and the electrodes from the damaging action of environmental agents such as oxygen and water.

Within this aim, an object of the present invention is to solve the above described problem by means of an encapsulant whose characteristics make it suitable to cover effectively organic electroluminescent devices, i.e.:

-- insolubility in common organic solvents, such as chlorinated solvents, benzene, toluene, xylene, cyclohexane, acetone, ethanol and methanol;

-- insolubility in water;

-- the possibility to be deposited with vacuum sublimation techniques, avoiding manipulations and passages that can introduce oxygen, water or other contaminants;

-- a glass transition temperature preferably above 100 °C.

Within this aim, an object of the present invention is to provide a structure that is relatively easy to provide in practice, safe in use, effective in operation, and relatively low in cost.

This aim and these and other objects which will become better apparent hereinafter are all achieved by the present encapsulant for organic electroluminescent devices of the type deposited on a supporting substrate and composed of at least two electrodes between which an electroluminescent substance is arranged, characterized in that said encapsulant is formed by at least one first inner layer, which is in direct contact with said electroluminescent device, which is constituted by an organic compound of the type of, or selected from quinacridones, acridones, and derivatives of perilene, said organic component being suitable to isolate said electroluminescent device from said atmospheric deteriorants.

An additional layer is also used which is superimposed on the preceding ones and is constituted by a hydrophobic polymeric component such as polycarbonate.

<u>Brief description of the drawings</u>

Further features will become better apparent from the detailed description of a preferred but not exclusive embodiment of a protective encapsulation for organic electroluminescent devices according to the invention, illustrated

only by way of non-limitative example in the accompanying drawings, wherein:

Figure 1 is a partially sectional perspective view of the encapsulant of the organic electroluminescent device;

Figure 2 is a sectional view of the electroluminescent device and of the encapsulant of Figure 1 taken along a first sectional plane;

Figure 3 is a sectional view of the electroluminescent device and of the encapsulant of Figure 1, taken along a second sectional plane;

Figure 4 is the structural formula of the quinacridones used in the present encapsulant;

Figure 5 is the structural formula of the acridones used in replacement of the quinacridones of Figure 4;

Figures 6 and 7 are the structural formulas of the perilene derivatives used in replacement of the quinacridones of Figure 4.

Ways to carrying out the Invention

With reference to the figures, the reference numeral 1 generally designates a protective encapsulation for organic electroluminescent devices according to the invention.

As shown more clearly in Figure 1, the encapsulant 1 is constituted by an inner layer 2 composed of three superimposed layers 2A, 2B, 2C and of an additional outer layer 3, which seals the electroluminescent device 4. The encapsulant 1 covers the electroluminescent device 4, which is in turn constituted by two superimposed layers of active organic material 4A, 4B comprised between a first electrode 5 and a second electrode 6.

The electrode 5 is composed of a series of bands of conducting material which are mutually parallel and adhere both to the supporting layer 7 and to the layer 4A of active organic material. The electrode 6 is instead composed of a series of mutually parallel bands arranged at right angles to the bands of the electrode 5.

Each band of the electrode 6 is composed of a first layer 6A and of a

second layer 6B, which are superimposed and adhere respectively to the layer 4B of the device 4 and to the first layer 2A of the encapsulant 1.

The layers 2A, 2C of the encapsulant 1 are constituted by organic material, while the layer 2B is made of a mixture of organic material and gas-absorbent material in percentages varying from 0 to 100%, i.e., the absorbent material can be present to the extent of constituting all of said mixture.

The absorbent material, used to capture any molecules of water and oxygen, is composed of metallic calcium.

The deposition of the layers 2A, 2B, 2C of the encapsulant 1 occurs by vacuum evaporation of the organic material and of the absorbent material.

The total thickness of the layers that constitute the inner layer 2 of the encapsulant 1 has a minimum limit of effectiveness approximately around 300-500 nm. The encapsulant organic material used for the inner layer 2 is constituted by molecules such as quinacridones.

The outer layer 3 of the encapsulant 1 is constituted by a hydrophobic polymer such as polycarbonate.

The outer layer 3 is applied to the inner layer 2 by using various methods: spin-coating, spray-coating, lamination, coating by immersion and screen printing.

For the sake of clarity, some examples of embodiment of OLED devices and of their encapsulation are given hereinafter. The durability tests of the encapsulated OLED devices were performed by periodically testing their operation in temperature and relative humidity conditions of 20-24 °C and 55-60% respectively.

EXAMPLE 1

An electroluminescent device 4 was produced in the following manner:

a) a glass plate coated with a layer of indium and tin oxide (ITO) with a thickness of approximately 100 nm, with the property of being transparent to light, was used as supporting layer 7. The plate was

cleaned chemically by immersing it in solutions of acetone and ethyl alcohol brought to a boil, and was then placed in an ultrasound washing unit for approximately 30 minutes.

b) this was followed by the deposition of the two active organic layers 4A and 4B on the electrode 5 of ITO, using an evaporator which operated with a vacuum of 10^{-6} mm Hg.

   I) a first layer 4A of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine, also known by the acronym TPD, with a thickness of 60 nm;

   II) a second layer 4B of tris-8-(hydroxyquinoline)-aluminum(III), also known by the acronym Alq3, with a thickness of 60 nm;

c) subsequent deposition of the second electrode 6:

   I) layer 6A of metallic calcium with a thickness of 25 nm

   II) a layer 6B of metallic silver with a thickness of 100 nm, acting as protection and electrical contact.

At first, the electroluminescent device 4 thus fabricated exhibits uniform emission on the entire active surface; non-emissive regions are noted 5 hours after fabrication.

EXAMPLE 2

An electroluminescent device 4 produced as in Example 1 is then coated, by high-vacuum deposition, by a layer 2A of quinacridone with a thickness of 200 nm.

The electroluminescent device thus fabricated exhibits at first uniform emission on its entire active surface; 48 hours after fabrication, non-emissive regions are noted.

EXAMPLE 3

An electroluminescent device 4, provided as in Example 1, is then coated by high-vacuum deposition with a layer 2A of quinacridone with a thickness of 600 nm. The resulting electroluminescent device at first exhibits uniform emission on its entire active surface; non-emissive regions are noted 30 days

after fabrication.

EXAMPLE 4

An electroluminescent device 4 as in Example 1 is then coated by high-vacuum deposition by a layer 2A of quinacridone with a thickness of 1200 nm.

The electroluminescent device thus fabricated exhibits at first uniform emission on its entire active surface; non-emissive regions are noted 110 days after fabrication.

EXAMPLE 5

An OLED device fabricated as in Example 1 is then coated, by high-vacuum deposition, by a layer 2A of quinacridones with a thickness of 1200 nm and by a layer 3 of polycarbonate.

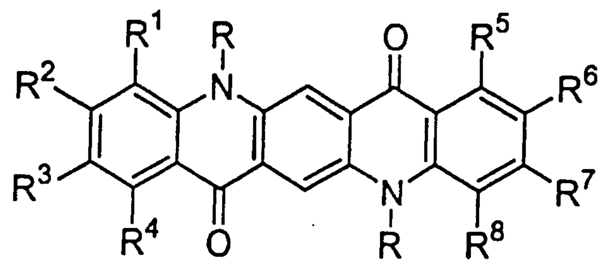
The electroluminescent device thus fabricated exhibits at first uniform emission on its entire active surface; non-emissive regions are noted 150 days after fabrication.

EXAMPLE 6

An OLED device fabricated as in Example 1 is then coated, by high-vacuum deposition, with a layer 2A which is constituted by quinacridone with a thickness of approximately 200 nm, with a layer 2B constituted by metallic calcium (absorbent) with a thickness of approximately 1000 nm, with a layer 2C constituted by quinacridone with a thickness of approximately 300 nm, and finally with an outer layer 3 of polycarbonate with a thickness of 1500 nm.

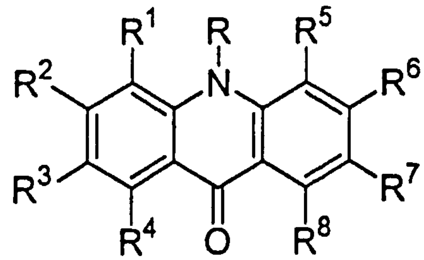
The electroluminescent device thus fabricated exhibits at first uniform emission on its entire active surface, and non-emissive regions are still not noted 180 days after fabrication.

Figure 4 illustrates the structural formula of the quinacridones used.



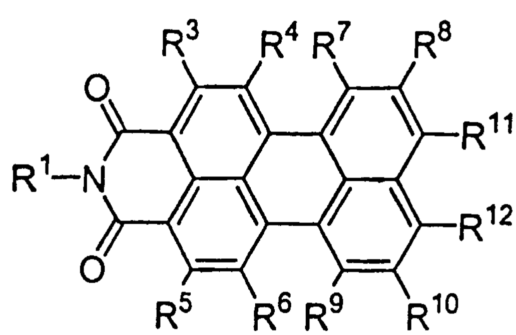
In particular, in relation to said Figure 4, the groups R1, R2, ..., R8 are each independently an atom of hydrogen, a halogen, an alkyl group or an alkoxy group, and R is independently a hydrogen or an alkyl group.

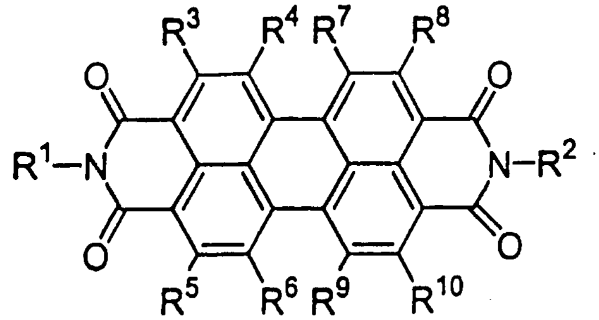
Figure 5 illustrates the structural formula of the compounds, acridones, used as an alternative to quinacridones, which are preferable.



In particular, in relation to said Figure 5, the groups R1, R2, ..., R8 are each independently an atom of hydrogen, a halogen, an alkyl group or an alkoxy group, and R is a hydrogen or an alkyl group.

Figures 6 and 7 illustrate the structural formulas of the compounds, perilene derivatives, used as an alternative to quinacridones, which are preferable.





In particular, in relation to said Figures 6 and 7, the groups R1 and R2 are independently a hydrogen, an alkyl, a phenyl, a naphthyl, and R3, R4, ..., R10 can be each independently a hydrogen or an alkyl.

Finally, as a replacement of metallic calcium, which is preferable, it is possible to deposit alternatively an alkaline metal, an alkaline earth metal, an alkaline metal oxide, an alkaline earth metal oxide, an alkaline metal sulfide, an alkaline earth metal sulfide, an alkaline metal chloride, an alkaline earth metal chloride.

An advantage of the present invention is the use of organic material, optionally mixed with an absorbent, deposited by means of the same deposition methods as the active layers and the electrodes. In this manner, it is possible to provide the first encapsulation process *in situ,* i.e., in the same place where the device is fabricated, avoiding manipulations and passages that might introduce oxygen, water or other contaminants.

This encapsulation further protects the active layers, allowing the deposition of a contiguous polymeric layer as an additional protection, also from a mechanical standpoint, of the device.

It has thus been shown that the invention achieves the intended aim and objects.

The shapes and the dimensions may be any according to requirements without thereby abandoning the scope of the protection of the appended claims.

The disclosures in Italian Patent Application No. BO2001A000066 from

which this application claims priority are incorporated herein by reference.

CLAIMS

1. An encapsulant for organic electroluminescent devices of the type deposited on a supporting substrate (7) and comprising at least two electrodes (5,6) between which an electroluminescent substance is arranged, characterized in that said encapsulant (1) is formed by at least one first inner layer (2,2A,2B,2C), which is in direct contact with said electroluminescent device (4), constituted by an organic compound of the type of, or selected from quinacridones, acridones, and derivatives of perilene, said organic component being suitable to isolate said electroluminescent device from atmospheric agents.

2. The encapsulant according to claim 1, characterized in that the first inner layer (2B) can comprise an inorganic component such as an alkaline metal, an alkaline earth metal, an alkaline metal oxide, an alkaline earth metal oxide, an alkaline metal sulfide, an alkaline earth metal sulfide, an alkaline metal chloride, an alkaline earth metal chloride, said inorganic component being suitable to chemically bond with said atmospheric agents in order to protect said electroluminescent device (4).

3. The encapsulant according to one or more of the preceding claims, characterized in that it comprises at least one second outer layer (3) which covers said first inner layer (2) and is composed of a hydrophobic polymer suitable to seal and protect said inner layer (2) from direct contact with said atmospheric agents.

4. The encapsulant according to one or more of the preceding claims, characterized in that said organic component of said first inner layer (2) is quinacridone.

5. The encapsulant according to one or more of the preceding claims, characterized in that said inorganic component of said inner layer (2) is calcium.

6. The encapsulant according to one or more of the preceding claims, characterized in that said hydrophobic polymer that constitutes said second

outer layer (3) is polycarbonate.

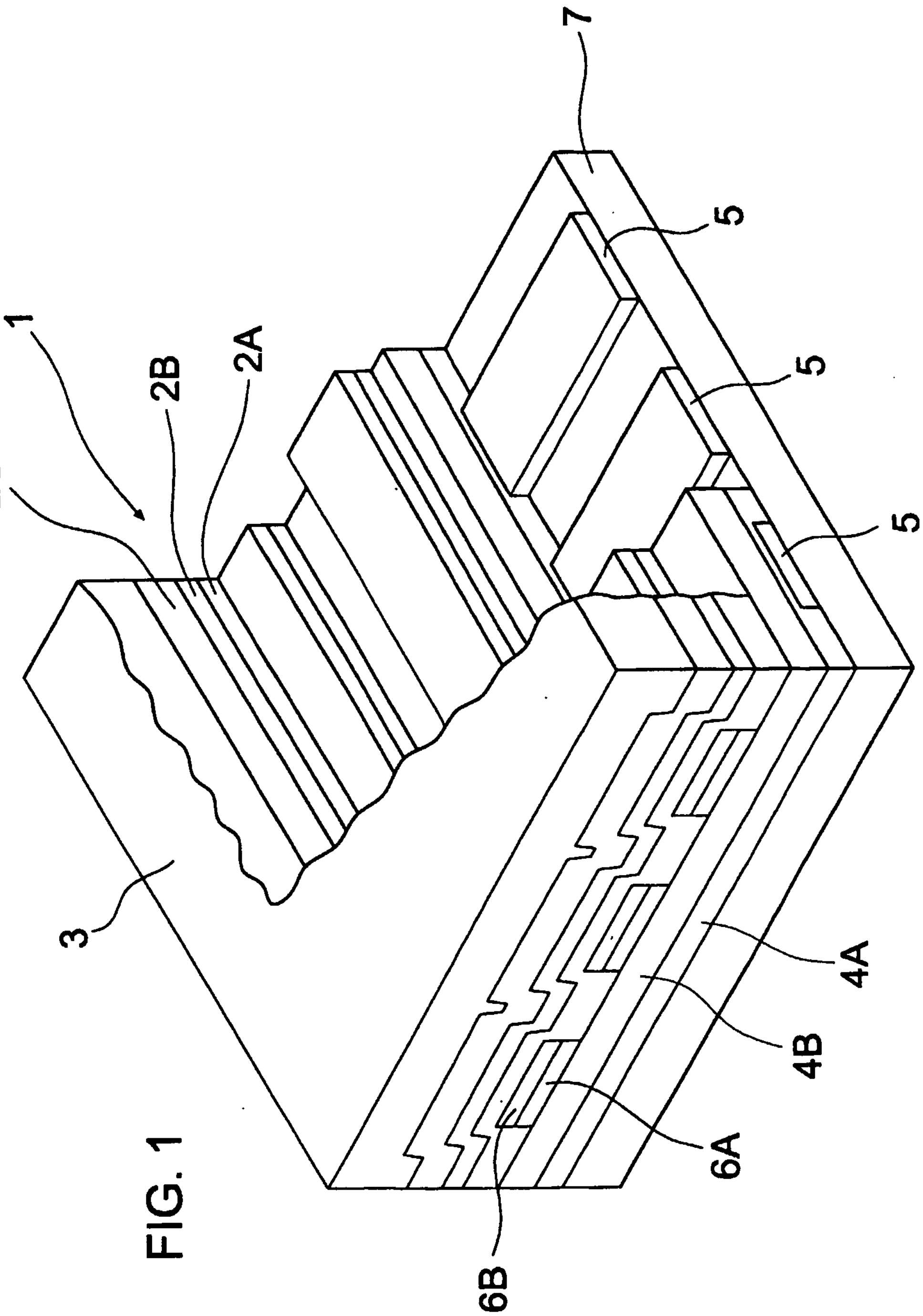


FIG. 1

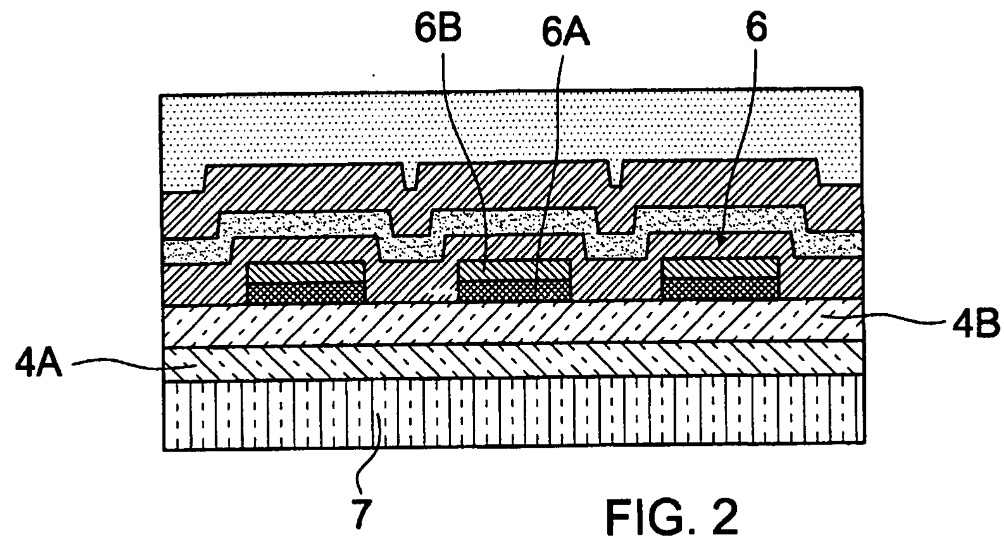


FIG. 2

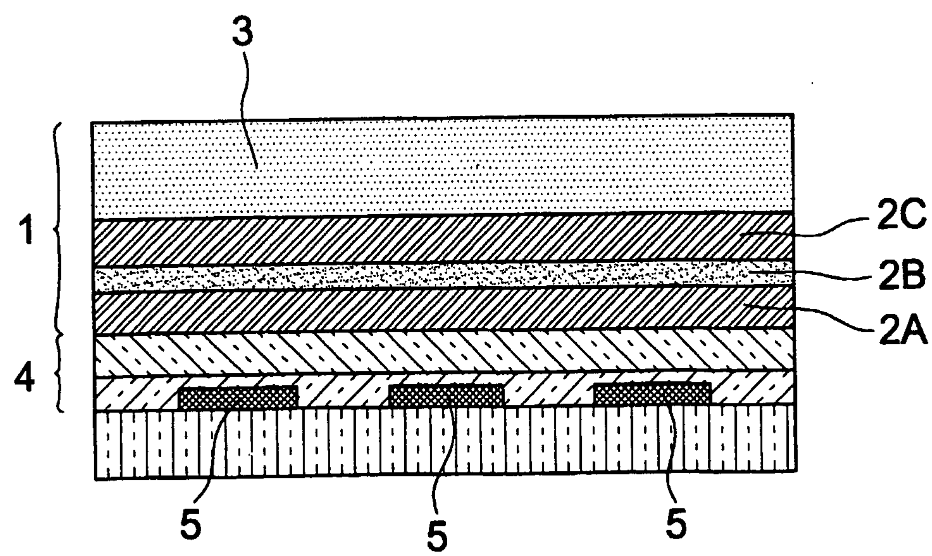


FIG. 3

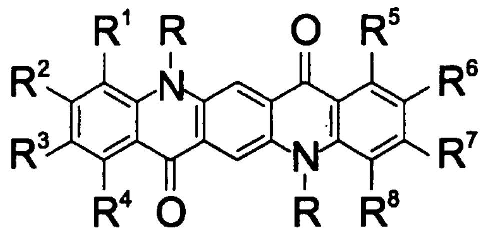
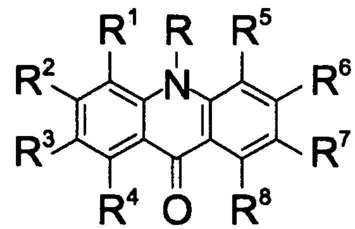


FIG. 4

FIG.5



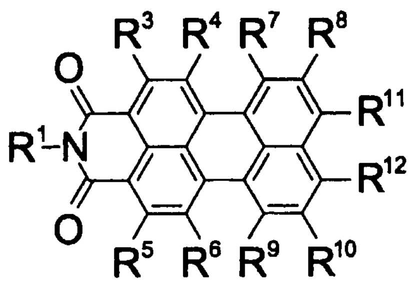
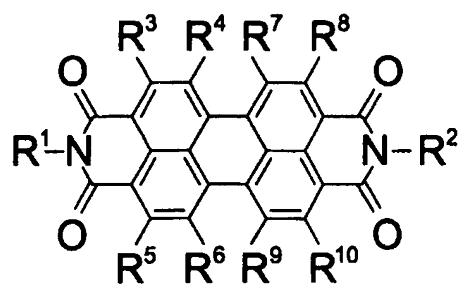


FIG. 6

FIG. 7



INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L33/00 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 952 778 A (HASKAL ELIAV ET AL) 14 September 1999 (1999-09-14) the whole document	1-8
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 450 (E-1416), 18 August 1993 (1993-08-18) & JP 05 101886 A (TDK CORP), 23 April 1993 (1993-04-23) abstract	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
27 May 2002	05/06/2002

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	BURROWS P E ET AL: "RELIABILITY AND DEGRADATION OF ORGANIC LIGHT EMITTING DEVICES" APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 65, no. 23, 5 December 1994 (1994-12-05), pages 2922-2924, XP000483815 ISSN: 0003-6951 abstract ---	
A	WO 99 31741 A (IBM) 24 June 1999 (1999-06-24) abstract -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/01134

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5952778	A	14-09-1999	TW	424406	B	01-03-2001
JP 05101886	A	23-04-1993	JP	3197306	B2	13-08-2001
WO 9931741	A	24-06-1999	WO	9931741	A1	24-06-1999